10 Rec'd PCT/FTO 9.3 APR 2002 10/089852

WO 01/25383

- 1 -

# FABRIC SOFTENER COMPOSITIONS

#### FIFLD OF THE INVENTION

The present invention relates to the use of fabric softener compositions comprising selected polyorganosiloxanes, or mixtures thereof, together with selected additives for the improvement of hydrophilicity properties of textile materials in domestic applications. In particular it relates to textile softening compositions for use in a textile laundering operation to impart excellent hydrophilicity properties on the textile.

### BACKGROUND OF THE INVENTION

The present invention relates to a method for increasing hydrophilicity of a fabric material. More particularly, the invention relates to a method for imparting a durably increased capacity of water absorption and a durably decreased susceptibility to accumulation of static electricity.

Needless to say, fabric materials currently on use both in the clothing use of people and in the industrial applications are in a very large part produced of synthetic fibers or traditional natural fibers. One of the largest differences between the properties of the synthetic and natural fibers is in the hydrophilicity-hydrophobicity behavior of them, the former fibers being of course outstandingly less hydrophilic than the latter. The remarkably small hydrophilicity of synthetic fibers sometimes causes serious problems not encountered in the use of natural fibers.

For example, fabric materials made of synthetic fibers have a very poor capacity of water or sweat absorption, which is advantageous on one hand but disadvantageous on the other, so that wearers of clothes made of synthetic fibers unavoidably have an unpleasant feeling of heavy stuffiness especially when the clothes are underwears worn in contact with or in the proximity of the skin of the wearer in a hot and humid climate.

Another serious problem caused by the poor hydrophilicity of synthetic fibers is the great accumulation of static electricity on the fibers causing unpleasantness to the wearer of clothes of synthetic fibers in such a charged condition.

Many attempts have of course been proposed and practiced in the prior art to solve these problems by increasing the hydrophilicity of the fabric materials of synthetic fibers and also natural fibres. For example, the problem of poor water absorption of synthetic fibers can be mitigated by the mixed spinning or mixed weaving with water-absorptive natural fibers. The effectiveness of this method is, however, limited since too much amounts of the natural fibers mixed with the synthetic fibers to attain sufficient hydrophilicity of the fabric material naturally result in the loss of the advantages inherent to synthetic fibers. An alternative method is the treatment of the fabric material of synthetic fibers with a water-absorbent agent to impart hydrophilicity to the surface of the fibers. Extensive investigations have been and are being undertaken in this direction to propose various kinds of water-absorbent agents effective for a particular type of synthetic fibers. For example, the capacity of water absorption of polyester fibers, e.g. polyethylene terephthalate fibers, can be increased by the treatment with a water-soluble polyester resin. Unfortunately, such a method of the treatment of synthetic fibers with a water-soluble resin is defective in several respects of the poor durability of the effects obtained therewith and the adverse influences on the color fastness of dved fabric materials in many cases.

Limiting the matter to the antistatic treatment or decrease of accumulation of static electricity on the synthetic fibers, various antistatic agents have been proposed hitherto. For example, the above mentioned water-soluble resins including water-soluble polyester resins, polyurethane resins, polyacrylamide resins, polyamide resins and the like are of course effective as an antistatic agent with certain durability. Besides, many compounds are known to be effective as an antistatic agent including inorganic salts such as calcium chloride and lithium chloride, guanidine compounds such as guanidine hydrochloride, surface active agents such as those of the types of quaternary ammonium salts and phosphoric acid esters, acrylic polymers having quaternary cationic groups and the like although the effectiveness of the treatment with these compounds is rather temporary.

The durability of the effects obtained with the above described antistatic agents is, however, not quite satisfactory even with the relatively durable polymeric antistatic agents and the antistatic effects obtained therewith are decreased in the long-run use of the treated fabric materials even by setting aside the other problem of the insufficient effectiveness of the method. Furthermore, the method is also not free from the problem of the decreased color

fastness of dyed fabric materials giving limitations to the amount and the manner of use of the antistatic agents.

In short, none of the prior art methods by use of a hydrophilic agent, i.e. water-absorbent agent or antistatic agent, is quite satisfactory for imparting hydrophilicity to the fabric materials in respects of the effectiveness and the durability.

As given above one component of the compositions of the present invention are polyorganosiloxanes. Such compounds are known to be used on an industrial scale to finish fabrics by providing them with a permanent or semi-permanent finish aimed at improving their general appearance. Significant for these industrial fabric finishing processes is a co-called curing step generally involving temperatures in excess of 150°C often for periods of one hour or more. The object here is to form a chemical finish which resists destruction during subsequent cleaning/laundering of fabrics. This process of finishing is not carried out in domestic applications and accordingly one would not expect benefits of a comparable nature or magnitude from polyorganosiloxanes included as adjuncts in domestic softeners. Indeed, it is noteworthy that if the compounds of the current invention achieved a permanence associated with industrial textile finishing, problems associated with a cumulative build through the wash cycles could occur such as fabric discoloration and even in extremes an unpleasant feel to the wearer.

Surprisingly, it has been found that the use of selected polyorganositoxanes, or mixtures thereof, and selected additives in fabric softener compositions provide excellent hydrophilic effects when applied to fabrics during a textile laundry operation.

Similar benefits are noted when compositions of the current invention are incorporated into tumble dryer additives such as impregnates on sheets.

#### SUMMARY OF THE INVENTION

This invention relates to a method of use of a fabric softener composition for imparting hydrophilicity to textile fibre materials in domestic applications, which softener composition comprises:

A) a fabric softener:

- 4 -

- B) at least one additive selected from the group consisting of
  - a) a polyethylene, or a mixture thereof,
  - b) a fatty acid alkanolamide, or a mixture thereof,
  - c) a polysiticic acid, or a mixture thereof, and
  - d) a polyurethane, or a mixture thereof; and
- C) a dispersed polyorganosiloxane of formula (1)

wherein

R1 is OH, OR2 or CH3

R2 is CH3 or CH2CH3

R3 is C1-C20alkoxy, CH3, CH2CHR4CH2NHR5, or CH2CHR4CH2N(COCH3)R5

(2) 
$$(CH_2)_3O$$
  $NR^8$   
or (3)  $(CH_2)_3NH$   $CH$   $NR^8$ 

R4 is H or CH3

R5 is H, CH2CH2NHR6, C(=O)-R7 or (CH2)z-CH3

z is 0 to 7

R<sup>6</sup> is H or C(≈O)-R<sup>7</sup>

R7 is CH3, CH2CH3 or CH2CH2CH2OH

R8 is H or CH3

the sum of X and Y is 40 to 4000;

or a dispersed polyorganosiloxane which comprises at least one unit of the formula (5)

wherein

R9 is CH3, CH3CH2 or Phenyl

R10 is -O-Si or -O-R9

the sum of v and w equals 3, and v does not equal 3

 $A = -CH_2CH(R^{11})(CH_2)_K$ 

 $B = -NR^{12}((CH_2)_1-NH)_mR^{12}$ , or

(6)

n is 0 or 1

when n is 0, U1 is N, when n is 1, U1 is CH

l is 2 to 8

k is 0 to 6

m is 0 to 3

R<sup>11</sup> is H or CH<sub>3</sub>

R12 is H, C(=O)-R16, CH2(CH2)0CH3 or

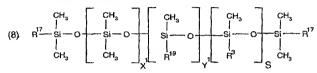
p is 0 to 6

R13 is NH, O, OCH2CH(OH)CH2N(Butyl), OOCN(Butyl)

- 6 -

 $R^{14}$  is H, linear or branched  $C_1$ - $C_4$  alkyl, Phenyl or  $CH_2CH(OH)CH_3$   $R^{15}$  is H or linear or branched  $C_1$ - $C_4$  alkyl  $R^{16}$  is  $CH_3$ ,  $CH_2CH_3$  or  $(CH_2)_qOH$ q is 1 to 6  $U^2$  is N or CH:

or a dispersed polyorganosiloxane of the formula (8)



### wherein

R3 is as previously defined

R<sup>17</sup> is OH, OR<sup>18</sup> or CH<sub>3</sub>

R18 is CH2 or CH2CH2

R19 is R20-(EO)m-(PO)n-R21

m is 3 to 25

n is 0 to 10

R20 is the direct bond or CH2CH(R22)(CH2)2R23

p is 1 to 4

R21 is H, R24, CH2CH(R22)NH2 or CH(R22)CH2NH2

R<sup>22</sup> is H or CH₃

R23 is O or NH

R24 is linear or branched C1-C8 alkyl or Si(R25)3

R25 is R24, OCH3 or OCH2CH3

EO is -CH2CH2O-

PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)O-

the sum of X<sub>1</sub>,Y<sub>1</sub> and S is 20 to 1500;

or a dispersed polyorganosiloxane of the formula (9)

-7-

wherein

R26 is linear or branched C1 - C20 alkoxy, CH2CH(R4)R29

R4 is as previously defined

R29 is linear or branched C1 - C20 alkyl

 $R^{27}$  is aryl, aryl substituted by linear or branched  $C_1$  -  $C_{10}$  alkyl, linear or branched  $C_1$  -  $C_{20}$  alkyl substituted by aryl or aryl substituted by linear or branched  $C_1$  -  $C_{10}$  alkyl  $R^{28}$  is

the sum of  $X^2$ ,  $X^3$ ,  $X^4$  and  $Y^2$  is 20 to 1500, wherein  $X^3$ ,  $X^4$  and  $Y^2$  may be independently of each other 0;

or a mixture thereof.

The composition is preferably used as a liquid rinse conditioner composition. The textile fibre materials are treated for hydrophilicity.

In tumble dryer applications the compositions are usually incorporated into impregnates on non-woven sheets. However, other application forms are known to those skilled in the art.

The fabric softener composition (especially in liquid form) will be used after the textile fibre materials have been washed with a laundry detergent, which may be one of a broad range of detergent types. The tumble dryer sheet will be used after a laundering process. The textile fibre materials may be damp or dry.

The fabric softener composition may also be sprayed directly onto the fabrics prior to or during the ironing or drying of the treated fabrics.

The polyorganosiloxane may be anionic, nonionic or cationic, preferably nonionic or cationic.

The polyorganosiloxanes, or mixtures thereof, are used in a dispersed form, via the use of an emulsifier. The fabric softener composition is preferably in aqueous liquid form. The water content as a rule is 25 to 90% by weight based on the total weight of the composition.

When the polyorganosiloxane contains a nitrogen atom, the nitrogen content of the aqueous emulsion due to the polyorganosiloxane is preferably from 0.001 to 0.25 % with respect to the silicon content. In general, a nitrogen content from 0.001 to 0.25 % is preferred. The particles of the emulsion as a rule have a diameter of between 5nm and 1000nm.

The fabric softener composition preferably has a solids content of 5 to 70% at a temperature of 120°C.

The fabric softener composition usually has a pH value from 2.0 to 7.0, especially 2.0 to 5.0.

The fabric softener composition may further comprise an additional polyorganosiloxane:

wherein g is

and G is C1 to C20 alkyl.

This polydimethylsiloxane is cationic, has a viscosity at 25°C of 250 mm<sup>2</sup>s<sup>-1</sup> to 450 mm<sup>2</sup>s<sup>-1</sup>, has a specific gravity of 1.00 to 1.02 g/cm<sup>3</sup> and has a surface tension of 28.5 mNm<sup>-1</sup> to 33.5 mNm<sup>-1</sup>.

The fabric softener composition may further comprise an additional polyorganosiloxane, such as that known as Magnasoft HSSD, or a polyorganosiloxane of the formula:

-9-

(13) 
$$H_3C - Si - O - Si - CH_3 - CH_3$$

R is  $CH_2CH_2CH_2N(R^-)_2$  R is linear or branched  $C_1-C_4$  alkyl R is  $(CH_2)_{X^-}(EO)_{m^-}(PO)_{n^-}R^$  m is 3 to 25 n is 0 to 10 X is 0 to 4 R''' is H or linear or branched  $C_1-C_4$  alkyl EO is  $-CH_2CH_2O$ - PO is  $-CH_2CH_2O$ - or  $-CH_2CH(CH_3)O$ the sum of X, Y and S is 40 to 300.

Preferably the compositions comprise dispersed polyorganosiloxanes of formula (1):

(1) 
$$R' = S_1 - O = S_1 - O = S_1 - O = S_2 - O = S_3 - O = S_4 - O = S_4 - O = S_4 - O = S_5 - CH_3$$

$$CH_3 = CH_3 = CH_$$

wherein

R1 is OH, OR2 or CH3

R2 is CH3 or CH2CH3

R3 is C1-C20alkoxy, CH3, CH2CHR4CH2NHR5, or

- 10 -

 $R^4$  is H or CH<sub>3</sub>  $R^5$  is H, CH<sub>2</sub>CH<sub>2</sub>NHR<sup>6</sup>, C(=O)-R<sup>7</sup>  $R^6$  is H or C(=O)-R<sup>7</sup>  $R^7$  is CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub> or CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH  $R^8$  is H or CH<sub>3</sub>

the sum of X and Y is 40 to 4000, especially 40 to 2000;

or a dispersed polyorganosiloxane which comprises at least one unit of the formula (5);

wherein

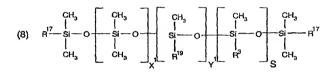
(6)

 $R^9$  is  $CH_3$ ,  $CH_3CH_2$   $R^{10}$  is -O-Si or -O- $R^9$ the sum of v and w equals 3, and v does not equal 3  $A = -CH_2CH(R^{11})(CH_2)_K$ B =

- 11 -

n is 1
U³ is CH
k is 0 to 6
R³¹ is H or CH₃
R³³ is OOCN(Butyl)
R³⁴ is H, linear C₁-C₄ alkyl, Phenyl
R³⁵ is H or linear C₁-C₄ alkyl
U² is N:

or a dispersed polyorganosiloxane of the formula (8);



# wherein

 $R^3$  is as previously defined  $R^{17}$  is OH,  $OR^{18}$  or  $CH_3$   $R^{18}$  is  $CH_3$  or  $CH_2CH_3$   $R^{19}$  is  $R^{20}$ -(EO)<sub>m</sub>-(PO)<sub>n</sub>- $R^{21}$  m is 3 to 25 n is 0 to 10  $R^{20}$  is the direct bond or  $CH_2CH(R^{22})(CH_2)_pR^{23}$  p is 1 to 4

 $R^{21}$  is H,  $R^{24},$   $CH_2CH(R^{22})NH_2$  or  $CH(R^{22})CH_2NH_2$   $R^{22}$  is H or  $CH_3$ 

R<sup>23</sup> is O or NH

 $\mathsf{R}^{24}$  is linear or branched  $\mathsf{C}_1\text{-}\mathsf{C}_3$  alkyl or  $\mathsf{Si}(\mathsf{R}^{25})_3$ 

R<sup>25</sup> is R<sup>24</sup>, OCH<sub>3</sub> or OCH<sub>2</sub>CH<sub>3</sub>

EO is -CH2CH2O-

PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)O-

the sum of X1,Y1 and s is 20 to 1500;

or a dispersed polyorganosiloxane of the formula (9);

 $R^{26}$  is linear  $C_1$  -  $C_{20}$  alkoxy,  $R^4$  is as previously defined  $R^{29}$  is linear  $C_1$  -  $C_{20}$  alkyl  $R^{27}$  is,  $CH_2CH(R^4)$ Phenyl  $R^{28}$  is

the sum of  $X^2$ ,  $X^3$ ,  $X^4$  and  $Y^2$  is 20 to 1500, wherein  $X^3$ ,  $X^4$  and  $Y^2$  may be independently of each other 0; or a mixture thereof.

The fabric softener composition may further comprise an additional polyorganosiloxane:

wherein g is

and G is C1 to C20 alkyl.

This polydimethylsiloxane is cationic, has a viscosity at 25°C of 250 mm²s¹ to 450 mm²s¹, has a specific gravity of 1.00 to 1.02 g/cm³ and has a surface tension of 28.5 mNm¹ to 33.5 mNm¹.

As to the polyorganosiloxanes of formula (1) the following preferences apply:

R1 is preferably OH or CH3.

R3 is preferably CH3, C10-C20alkoxy or CH2CHR4CH2NHR5.

R4 is preferably H.

R5 is preferably H or CH2CH2NHR6.

R<sup>6</sup> is preferably H or C(=0)-R<sup>7</sup>.

R7 is preferably CH3, CH2CH3 or especially CH2CH2CH2OH.

The sum of X + Y is preferably 100 to 2000.

Preferred are polyorganosiloxanes of formula (1) wherein

R1 is OH or CH3.

R3 is CH3, C10-C20alkoxy or CH2CHR4CH2NHR5,

R4 is H.

R5 is H or CH2CH2NHR6,

R<sup>6</sup> is H or C(=O)-R<sup>7</sup>, and

R<sup>7</sup> is CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub> or especially CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH.

As to the polyorganosiloxanes of formula (8) the following preferences apply:

R3 is preferably CH3, C10-C20alkoxy or CH2CHR4CH2NHR5.

R<sup>4</sup> is preferably H.

R5 is preferably H or CH2CH2NHR6.

R<sup>5</sup> is preferably H or C(=0)-R<sup>7</sup>.

R7 is preferably CH2CH3, CH2CH2CH2OH or especially CH3.

R<sub>17</sub> is preferably CH<sub>3</sub> or OH.

R<sub>20</sub> is preferably the direct bond.

R<sub>21</sub> is preferably H.

Preferred are polyorganosiloxanes of formula (8) wherein

R3 is CH3, C10-C20alkoxy or CH2CHR4CH2NHR5,

- 14 -

R<sup>4</sup> is H, R<sup>5</sup> is H or CH<sub>2</sub>CH<sub>2</sub>NHR<sup>6</sup>, R<sup>6</sup> is H or C(=O)-R<sup>7</sup>, R<sup>7</sup> is CH<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>OH or especially CH<sub>3</sub>, and R<sub>17</sub> is CH<sub>3</sub> or OH.

As to the polyorganosiloxanes of formula (9) the following preferences apply:  $R^{26}$  is preferably  $CH_2CH(R^4)R^{29}$ .  $R^4$  is preferably H.  $R^{27}$  is preferably 2-phenyl propyl. The sum of  $X^2$ ,  $X^4$  and  $Y^2$  is preferably 40 to 500.

Preferred are polyorganosiloxanes of formula (9) wherein  $R^{26}$  is  $CH_2CH(R^4)R^{29}$ ,  $R^4$  is H, and  $R^{27}$  is 2-phenyl propyl.

Preferred are polyorganosiloxanes of formulae (1), (8) and (9), especially those of formulae (1) and (8). Very interesting polyorganosiloxanes are those of formula (1).

Emulsifiers used to prepare the polyorganosiloxane compositions include:

- i) Ethoxylates, such as alkyl ethoxylates, amine ethoxylates or ethoxylated alkylammoniumhalides. Alkyl ethoxylates include alcohol ethoxylates or isotridecyl ethoxylates. Preferred alcohol ethoxylates include linear or branched nonionic alkyl ethoxylates containing 2 to 15 ethylene oxide units. Preferred isotridecyl ethoxylates include nonionic isotridecyl ethoxylates containing 5 to 25 ethylene oxide units. Preferred amine ethoxylates include nonionic C10 to C20 alkyl amino ethoxylates containing 4 to 10 ethylene oxide units. Preferred ethoxylated alkylammoniumhalides include nonionic or cationic ethoxylated C6 to C20 alkyl bis(hydroxyethyl)methylammonium chlorides.
- ii) Alkylammonium halides, preferably cationic quaternary ester alkylammonium halides.
- iii) Silicones, preferably nonionic polydimethylsiloxane polyoxyalkylene copolymers
- iv) Saccharides, preferably nonionic alkylpolyglycosides.

A mixture of these emulsifiers may also be used.

As mentioned previously, the compositions further comprise one or more additives selected from polyethylene, dispersed fatty acid alkanol amide, polysilicic acid and polyurethane. These components are described below.

The emulsifiable polyethylene (polyethylene wax) is known and is described in detail in the prior art (compare, for example, DE-C-2,359,966, DE-A-2,824,716 and DE-A-1,925,993). The emulsifiable polyethylene is as a rule a polyethylene having functional groups, in particular COOH groups, some of which can be esterified. These functional groups are introduced by oxidation of the polyethylene. However, it is also possible to obtain the functionality by copolymerization of ethylene with, for example, acrylic acid. The emulsifiable polyethylenes preferably have a density of at least 0.91 g/cm³ at 20°C., an acid number of at least 5 and a saponification number of at least 10. Emulsifiable polyethylenes which have a density of 0.95 to 1.05 g/cm³ at 20°C, an acid number of 10 to 60 and a saponification number of 15 to 80 are particularly preferred. Polyethylenes which have a drop point of 100-150°C are preferred. This material is generally obtainable commercially in the form of flakes, lozenges and the like. A mixture of these emulsifiable polyethylenes may also be used.

The polyethylene wax is usually employed in the form of dispersions. Various emulsifiers are suitable for their preparation. The preparation of the dispersions is described in detail in the prior art.

Emulsifiers suitable for dispersing the polyethylene component include:

- i) Ethoxylates, such as alkyl ethoxylates or amine ethoxylates. Alkyl ethoxylates include alcohol ethoxylates or isotridecyl ethoxylates. Preferred alcohol ethoxylates include nonionic fatty alcohol ethoxylates containing 2 to 55 ethylene oxide units. Preferred isotridecyl ethoxylates include nonionic isotridecyl ethoxylates containing 6 to 9 ethylene oxide units. Preferred amine ethoxylates include nonionic C10 to C20 alkyl amino ethoxylates containing 7 to 9 ethylene oxide units.
- ii) Alkylammonium halides, preferably cationic quaternary ester alkylammonium halides.
- iii) Ammonium salts, preferably cationic aliphatic quaternary ammonium chloride or sulfate.

A mixture of these emulsifiers may also be used.

Suitable fatty acid alkanolamides are for example those of formula

### wherein

R<sub>33</sub> is a saturated or unsaturated hydrocarbon radical containing 10 to 24 carbon atoms,

number from 1 to 10 and R<sub>36</sub> is as defined above for R<sub>33</sub>, and

c is as defined above.

 $R_{38}$ ,  $R_{39}$ ' and  $R_{38}$ " have the same or different meaning and are as defined above for  $R_{34}$ , and  $R_{39}$ ,  $R_{39}$ ' and  $R_{39}$ " have the same or different meaning and are a radical of formula

 $R_{33}$  and  $R_{36}$  are preferably a saturated or unsaturated hydrocarbon radical containing 14 to 24 carbon atoms. Preferred are saturated hydrocarbon radicals.

R<sub>34</sub> is preferably hydrogen, -CH₂OH or a radical of formula —C-R<sub>36</sub> Ras is preferably a radical of formula

As to R<sub>38</sub>, R<sub>38</sub> and R<sub>38</sub>" the preferences given above for R<sub>34</sub> apply.

c is preferably a number from 1 to 5.

Preferred are fatty acid alkanolamides of formula

wherein R<sub>33</sub>, R<sub>34</sub>, R<sub>38</sub>, R<sub>38</sub>, R<sub>38</sub>, R<sub>38</sub>, R<sub>39</sub>, R<sub>39</sub>, and R<sub>39</sub>" are as defined above.

Preferred are fatty acid alkanolamides of formula (15a), wherein R<sub>34</sub>, R<sub>38</sub>, R<sub>38</sub> and R<sub>38</sub>" are hydrogen or -CH<sub>2</sub>OH.

Furthermore, fatty acid alkanolamides of formula

- 18 -

are preferred, wherein R<sub>33</sub>, R<sub>34</sub>, R<sub>37</sub> and c are as defined above.

Preferred are fatty acid alkanolamides of formula (15b), wherein

 $R_{34}$  and  $R_{37}$  are hydrogen or a radical of formula  $\begin{bmatrix} 0 \\ -C - R_{se} \end{bmatrix}$ .  $R_{34}$  is preferably hydrogen.

The above fatty acid alkanolamides can also be present in form of the corresponding ammonium salts.

A mixture of these fatty acid alkanolamides may also be used.

Emulsifiers suitable for dispersing the fatty acid alkanol amide component include:

- i) Ethoxylates, such as alkyl ethoxylates, amine ethoxylates or amide ethoxylates. Alkyl ethoxylates include alcohol ethoxylates or isotridecyl ethoxylates. Preferred alcohol ethoxylates include nonionic fatty alcohol ethoxylates containing 2 to 55 ethylene oxide units. Preferred isotridecyl ethoxylates include nonionic isotridecyl ethoxylates containing 5 to 45 ethylene oxide units. Preferred amine ethoxylates include nonionic C10 to C20 alkyl amino ethoxylates containing 4 to 25 ethylene oxide units. Preferred amide ethoxylates include cationic fatty acid amide ethoxylates containing 2 to 25 ethylene oxide units.
- ii) Alkylammonium halides, preferably cationic quaternary ester alkylammonium halides or cationic aliphatic acid alkylamidotrialkylammonium methosulfates.
- iii) Ammonium salts, preferably cationic aliphatic quaternary ammonium chloride or sulfate.

A mixture of these emulsifiers may also be used.

Examples for polyurethanes are the reaction products of a diol and an ethoxysilate with a diisocyanate.

The additives selected from the group consisting of a polyethylene, a fatty acid alkanolamide, a polysilicic acid, and a polyurethane are, as a rule, used in an amount of 0.01 to 25 % by weight, especially 0.01 to 15 % by weight, based on the total weight of the fabric

- 19 -

softener composition. An amount of 0.05 to 15 % by weight, especially 0.1 to 15 % by weight, is preferred. Highly preferred is an upper limit of 10 %, especially 5 %.

Preferred as additives are polyethylene, fatty acid alkanolamides and polyurethanes, especially polyethylene and fatty acid alkanolamides. Highly preferred are polyethylene.

A highly preferred fabric softener composition used according to the present invention comprises:

- a) 0.01 to 70 % by weight based on the total weight of the composition of a polyorganosiloxane, or a mixture thereof;
- b) 0.2 to 15 % by weight based on the total weight of an emulsifier, or a mixture thereof;
- c) 0.01 to 25 % by weight, especially 0.01 to 15 % by weight, based on the total weight of at least one additive selected from the group consisting of a polyethylene, a fatty acid alkanolamide, a polysilicic acid, or a polyurethane, and
- d) water to 100 %.

The fabric softener compositions can be prepared as follows:

Firstly, emulsions of the polyorganosiloxane are prepared. The polyorganosiloxane and polyethylene, fatty acid alkanol amide, polysilicic acid or polyurethane are emulsified in water using one or more surfactants and shear forces, e.g. by means of a colloid mill. Suitable surfactants are described above. The components may be emulsified individually before being mixed together, or emulsified together after the components have been mixed. The surfactant(s) is/are used in customary amounts known to the person skilled in the art and can be added either to the polyorganosiloxane or to the water prior to emulsification. Where appropriate, the emulsification operation can be carried out at elevated temperature. The fabric softener composition according to the invention is usually, but not exclusively, prepared by firstly stirring the active substance, i.e. the hydrocarbon based fabric softening component, in the molten state into water, then, where required, adding further desired additives and, finally, after cooling, adding the polyorganosiloxane emulsion.

The fabric softener composition can, for example, be prepared by mixing a preformulated fabric softener with an emulsion comprising the polyorganosiloxane and the additive.

- 20 -

The fabric softening components can be conventional hydrocarbon based fabric softening components known in the art.

Hydrocarbon fabric softeners suitable for use herein are selected from the following classes of compounds:

(i) Cationic quaternary ammonium salts. The counter ion of such cationic quaternary ammonium salts may be a halide, such as chloride or bromide, methyl sulphate, or other ions well known in the literature. Preferably the counter ion is methyl sulfate or any alkyl sulfate or any halide, methyl sulfate being most preferred for the dryer-added articles of the invention.

Examples of cationic quaternary ammonium salts include but are not limited to:

(1) Acyclic quaternary ammonium salts having at least two  $C_8$  to  $C_{30}$ , preferably  $C_{12}$  to  $C_{22}$  alkyl or alkenyl chains, such as: ditallowdimethyl ammonium methylsulfate, di(hydrogenated tallow)dimethyl ammonium methylsulfate, distearyldimethyl ammonium methylsulfate, dicocodimethyl ammonium methylsulfate and the like. It is especially preferred if the fabric softening compound is a water insoluble quaternary ammonium material which comprises a compound having two  $C_{12}$  to  $C_{18}$  alkyl or alkenyl groups connected to the molecule via at least one ester link. It is more preferred if the quaternary ammonium material has two ester links present. An especially preferred ester-linked quaternary ammonium material for use in the invention can be represented by the formula:

wherein each  $R^{3\tau}$  group is independently selected from  $C_1$  to  $C_4$  alkyl, hydroxyalkyl or  $C_2$  to  $C_4$  alkenyl groups; T is either

- 21 -

and wherein each  $R^{32}$  group is independently selected from  $C_{\theta}$  to  $C_{2\theta}$  alkyl or alkenyl groups; and e is an integer from 0 to 5.

A second preferred type of quaternary ammonium material can be represented by the formula:

A second preferred type of quaternary ammonium material can be represented by the formula:

(19) 
$$(R^{31})_3N^{+}$$
  $(CH_2)_e$   $CH_2OOR^{32}$ 

wherein R31, e and R32 are as defined above.

- (2) Cyclic quaternary ammonium salts of the imidazolinium type such as di(hydrogenated tallow)dimethyl imidazolinium methylsulfate, 1-ethylene-bis(2-tallow-1-methyl) imidazolinium methylsulfate and the like;
- (3) Diamido quaternary ammonium salts such as: methyl-bis(hydrogenated tallow amidoethyl)-2-hydroxethyl ammonium methyl sulfate, methyl bi(tallowamidoethyl)-2-hydroxypropyl ammonium methylsulfate and the like;
- (4) Biodegradable quaternary ammonium salts such as N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium methyl sulfate and N,N-di(tallowoyl-oxy-propyl)-N,N-dimethyl ammonium methyl sulfate. Biodegradable quaternary ammonium salts are described, for

- 22 -

example, in U.S. Patents 4,137,180, 4,767,547 and 4,789,491 incorporated by reference herein.

Preferred biodegradable quaternary ammonium salts include the biodegradable cationic diester compounds as described in U.S. Patent 4,137,180, herein incorporated by reference.

- (ii) Tertiary fatty amines having at least one and preferably two C8 to C30, preferably C12 to C22 alkyl chains. Examples include hardened tallow-di-methylamine and cyclic amines such as 1-(hydrogenated tallow)amidoethyl-2-(hydrogenated tallow) imidazoline. Cyclic amines which may be employed for the compositions herein are described in U.S. Patent 4,806,255 incorporated by reference herein.
- (iii) Carboxylic acids having 8 to 30 carbons atoms and one carboxylic group per molecule. The alkyl portion has 8 to 30, preferably 12 to 22 carbon atoms. The alkyl portion may be linear or branched, saturated or unsaturated, with linear saturated alkyl preferred. Stearic acid is a preferred fatty acid for use in the composition herein. Examples of these carboxylic acids are commercial grades of stearic acid and palmitic acid, and mixtures thereof which may contain small amounts of other acids.
- (iv) Esters of polyhydric alcohols such as sorbitan esters or glycerol stearate. Sorbitan esters are the condensation products of sorbitol or iso-sorbitol with fatty acids such as stearic acid. Preferred sorbitan esters are monoalkyl. A common example of sorbitan ester is SPAN 60 (ICI) which is a mixture of sorbitan and isosorbide stearates.
- (v) Fatty alcohols, ethoxylated fatty alcohols, alkyphenols, ethoxylated alkyphenols, ethoxylated fatty amines, ethoxylated monoglycerides and ethoxylated diglycerides.
- (vi) Mineral oils, and polyols such as polyethylene glycol.

These softeners are more definitively described in U.S. Patent 4,134,838 the disclosure of which is incorporated by reference herein. Preferred fabric softeners for use herein are acyclic quaternary ammonium salts. Di(hydrogenated)tallowdimethyl ammonium methylsulfate is most widely used for dryer articles of this invention. Mixtures of the above mentioned fabric softeners may also be used.

The fabric softening composition employed in the present invention contains as a rule about 0.1% to about 95% of the fabric softening component. Preferably from about 2% to about 70% and most preferably from about 2% to about 30% of the fabric softening component is employed herein to obtain optimum softening at minimum cost. When the fabric softening component includes a quaternary ammonium salt, the salt is used in the amount of about 2% to about 70%, preferably about 2% to about 30%.

The fabric softener composition may also comprise additives which are customary for standard commercial liquid rinse conditioners, for example alcohols, such as ethanol, n-propanol, i-propanol, polyhydric alcohols, for example glycerol and propylene glycol; amphoteric and nonionic surfactants, for example carboxyl derivatives of imidazole, oxyethylated fatty alcohols, hydrogenated and ethoxylated castor oil, alkyl polyglycosides, for example decyl polyglucose and dodecylpolyglucose, fatty alcohols, fatty acid esters, fatty acids, ethoxylated fatty acid glycerides or fatty acid partial glycerides; also inorganic or organic salts, for example water-soluble potassium, sodium or magnesium salts, non-aqueous solvents, pH buffers, perfumes, dyes, hydrotropic agents, antifoams, anti redeposition agents, polymeric or other thickeners, enzymes, optical brighteners, antishrink agents, stain removers, germlcides, fungicides, antioxidants and corrosion inhibitors.

These fabric softener compositions are traditionally prepared as dispersions containing for example up to 20 % by weight of active material in water. They have a turbid appearance. However, alternative formulations usually containing actives at levels of 5 to 40 % along with solvents can be prepared as microemulsions which have a clear appearance (as to the solvents and the formulations see for example US-A-5,543,067 und WO-A-98/17757). The additives and polyorganosiloxanes of the present invention can be used for such compositions although it will be necessary to use them in microemulsion form to preserve the clear appearance of the fabric softener compositions which are microemulsions.

Another aspect of the invention is a tumble dryer sheet article. The fabric softener composition of the present invention may be coated onto a flexible substrate which carries a fabric conditioning amount of the composition and is capable of releasing the composition at dryer operating temperatures. The conditioning composition in turn has a preferred melting (or softening) point of about 25°C to about 150°C.

The fabric softener composition which may be employed in the invention is coated onto a dispensing means which effectively releases the fabric conditioning composition in a tumble dryer. Such dispensing means can be designed for single usage or for multiple uses. One such multi-use article comprises a sponge material releasably enclosing enough of the conditioning composition to effectively impart fabric softness during several drying cycles. This multi-use article can be made by filling a porous sponge with the composition. In use, the composition melts and leaches out through the pores of the sponge to soften and condition fabrics. Such a filled sponge can be used to treat several loads of fabrics in conventional dryers, and has the advantage that it can remain in the dryer after use and is not likely to be misplaced or lost.

Another article comprises a cloth or paper bag releasably enclosing the composition and sealed with a hardened plug of the mixture. The action and heat of the dryer opens the bag and releases the composition to perform its softening.

A highly preferred article comprises the inventive compositions releasably affixed to a flexible substrate such as a sheet of paper or woven or non-woven cloth substrate. When such an article is placed in an automatic laundry dryer, the heat, moisture, distribution forces and tumbling action of the dryer removes the composition from the substrate and deposits it on the fabrics.

The sheet conformation has several advantages. For example, effective amounts of the compositions for use in conventional dryers can be easily absorbed onto and into the sheet substrate by a simple dipping or padding process. Thus, the end user need not measure the amount of the composition necessary to obtain fabric softness and other benefits. Additionally, the flat configuration of the sheet provides a large surface area which results in efficient release and distribution of the materials onto fabrics by the tumbling action of the dryer.

The substrates used in the articles can have a dense, or more preferably, open or porous structure. Examples of suitable materials which can be used as substrates herein include paper, woven cloth, and non-woven cloth. The term "cloth" herein means a woven or non-woven substrate for the articles of manufacture, as distinguished from the term "fabric"

- 25 -

which encompasses the clothing fabrics being dried in an automatic dryer.

It is known that most substances are able to absorb a liquid substance to some degree; however, the term "absorbent", as used herein, is intended to mean a substrate with an absorbent capacity (i.e., a parameter representing a substrates ability to take up and retain a liquid) from 4 to 12, preferably 5 to 7 times its weight of water.

If the substrate is a foamed plastics material, the absorbent capacity is preferably in the range of 15 to 22, but some special foams can have an absorbent capacity in the range from 4 to 12.

Determination of absorbent capacity values is made by using the capacity testing procedures described in U.S. Federal Specifications (UU-T-595b), modified as follows:

- 1. tap water is used instead of distilled water;
- 2. the specimen is immersed for 30 seconds instead of 3 minutes;
- 3. draining time is 15 seconds instead of 1 minute; and
- the specimen is immediately weighed on a torsion balance having a pan with turned-up edges.

Absorbent capacity values are then calculated in accordance with the formula given in said Specification. Based on this test, one-ply, dense bleached paper (e.g., Kraft or bond having a basis weight of about 32 pounds per 3,000 square feet) has an absorbent capacity of 3.5 to 4; commercially available household one-ply towel paper has a value of 5 to 6; and commercially available two-ply household towelling paper has a value of 7 to about 9.5.

Suitable materials which can be used as a substrate in the invention herein include, among others, sponges, paper, and woven and non-woven cloth, all having the necessary absorbency requirements defined above.

The preferred non-woven cloth substrates can generally be defined as adhesively bonded fibrous or filamentous products having a web or carded fiber structure (where the fiber strength is suitable to allow carding), or comprising fibrous mats in which the fibers or filaments are distributed haphazardly or in random array (i.e. an array of fibers is a carded web wherein partial orientation of the fibers is frequently present, as well as a completely

- 26 -

haphazard distributional orientation), or substantially aligned. The fibers or filaments can be natural (e.g. wool, silk, jute, hemp, cotton, linen, sisal, or ramie) or synthetic (e.g. rayon, cellulose ester, polyvinyl derivatives, polyolefins, polyamides, or polyesters).

The preferred absorbent properties are particularly easy to obtain with non-woven cloths and are provided merely by building up the thickness of the cloth, i.e., by superimposing a plurality of carded webs or mats to a thickness adequate to obtain the necessary absorbent properties, or by allowing a sufficient thickness of the fibers to deposit on the screen. Any diameter or denier of the fiber (generally up to about 10 denier) can be used, inasmuch as it is the free space between each fiber that makes the thickness of the cloth directly related to the absorbent capacity of the cloth, and which, further, makes the non-woven cloth especially suitable for impregnation with a composition by means of intersectional or capillary action. Thus, any thickness necessary to obtain the required absorbent capacity can be used.

When the substrate for the composition is a non-woven cloth made from fibers deposited haphazardly or in random array on the screen, the articles exhibit excellent strength in all directions and are not prone to tear or separate when used in the automatic clothes dryer.

Preferably, the non-woven cloth is water-laid or air-laid and is made from cellulosic fibers, particularly from regenerated cellulose or rayon. Such non-woven cloth can be lubricated with any standard textile lubricant.

Preferably, the fibers are from 5mm to 50mm in length and are from 1.5 to 5 denier. Preferably, the fibers are at least partially orientated haphazardly, and are adhesively bonded together with a hydrophobic or substantially hydrophobic binder-resin. Preferably, the cloth comprises about 70% fiber and 30% binder resin polymer by weight and has a basis weight of from about 18 to 45g per square meter.

In applying the fabric softener composition to the absorbent substrate, the amount impregnated into and/or coated onto the absorbent substrate is conveniently in the weight ratio range of from about 10:1 to 0.5:1 based on the ratio of total conditioning composition to dry, untreated substrate (fiber plus binder). Preferably, the amount of the conditioning composition ranges from about 5:1 to about 1:1, most preferably from about 3:1 to 1:1, by

- 27 -

weight of the dry untreated substrate.

According to one preferred embodiment of the invention, the dryer sheet substrate is coated by being passed over a rotogravure applicator roll. In its passage over this roll, the sheet is coated with a thin, uniform layer of molten fabric softening composition contained in a rectangular pan at a level of about 15g per square yard. Passage for the substrate over a cooling roll then solidifies the molten softening composition to a solid. This type of applicator is used to obtain a uniform homogeneous coating across the sheet.

Following application of the liquefied composition, the articles are held at room temperature until the composition substantially solidifies. The resulting dry articles, prepared at the composition substrate ratios set forth above, remain flexible; the sheet articles are suitable for packaging in rolls. The sheet articles can optionally be slitted or punched to provide a non-blocking aspect at any convenient time if desired during the manufacturing process.

The fabric softener composition employed in the present invention includes certain fabric softeners which can be used singly or in admixture with each other.

Examples of suitable textile fibre materials which can be treated with the fabric softener composition are materials made of silk, wool, polyamide, acrylics or polyurethanes, and, in particular, cellulosic fibre materials of all types. Such fibre materials are, for example, natural cellulose fibres, such as cotton, linen, jute and hemp, and regenerated cellulose. Preference is given to textile fibre materials made of cotton. The fabric softener compositions are also suitable for hydroxyl-containing fibres which are present in mixed fabrics, for example mixtures of cotton with polyester fibres or polyamide fibres.

A better understanding of the present invention and of its many advantages will be had by referring to the following Examples, given by way of illustration. The percentages given in the examples are percentages by weight.

Example 1 (preparation of the rinse conditioners)

The liquid rinse conditioners are prepared by using the procedure described below. This type of fabric rinse conditioners is normally known under the name of "triple strength" or "triple fold" formula.

75 % by weight of the total amount of water is heated to 40°C. The molten fabric softener di-(palmcarboxyethyl-)hydroxyethyl-methylammonium-methosulfate (or Rewoquat WE 38 DPG available from Witco) is added to the heated water under stirring and the mixture is stirred for 1 hour at 40°C. Afterwards the aqueous softener solution is cooled down to below 30°C while stirring. When the solution cools down sufficiently magnesium chloride is added and the pH is adjusted to 3.2 with 0.1 N hydrochloric acid. The formulation is then filled up with water to 100%.

The rinse conditioner formulation as described above was used as a base formulation. In a final step the fabric softener is mixed with a separately prepared polyorganosiloxane /additive emulsion. The fabric softener formulations used in the following examples are listed in the following Table 1.

Table 1 (rinse conditioner formulations used in the application test for 1 kg wash load)

Rinse conditioner	Polyorgano-siloxane	Fabric softener	pН
formulation	emulsion (calculated	Base Formulation	
	on solid content of		
	the emulsion)		
0 (Reference)		13.3 g	3.2
Α	0.2 g of Type I	13.3 g	3.2
В	0.2 g of Type II	13.3 g	3.2
С	0.2 g of Type III	13.3 g	3.2
D	0.2 g of Type IV	13.3 g	3.2
E	0.2 g of Type V	13.3 g	3.2
F	0.2 g of Type VI	13.3 g	3.2
G	0.2 g of Type VII	13.3 g	3.2
Н	0.2 g of Type VIII	13.3 g	3.2
ı	0.2 g of Type IX	13.3 g	3.2
J	0.2 g of Type X	13.3 g	3.2
К	0.2 g of Type XI	13.3 g	3.2
L	0.2 g of Type XII	13.3 g	3.2
М	0.2 g of Type XV	13.3 g	3.2

- 29 -

### Types of polyorganosiloxane emulsions used

## Type I

- Polyorganosiloxane of general formula (1), wherein R<sub>1</sub> is -OH, R<sub>3</sub> is -CH<sub>3</sub>,
- X + Y = 300-1500, % nitrogen (with respect to silicone) = 0
- 3.7% of an emulsifier
- 12.5% of an emulsifiable oxidised polyethylene which has a density of 0.95 to 1.05 g/cm³ at 20°C, a drop point of 100-150°C, an acid number of 10 to 60 and a saponification number of 15 to 80
- solid content of the emulsion measured by evaporation at 120°C = 27.0-29.0%
- water content = 71.3%

### Type II

- Polyorganosiloxane of general formula (1), wherein R<sub>1</sub> is -OH, R<sub>3</sub> is -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>,
- X + Y = 300-1500, % nitrogen (with respect to silicone) = 0.025
- 4.5% of an emulsifier
- 1% of an emulsifiable oxidised polyethylene which has a density of 0.95 to 1.05 g/cm<sup>3</sup> at 20°C, a drop point of 100-150°C, an acid number of 10 to 60 and a saponification number of 15 to 80
- solid content of the emulsion measured by evaporation at 120°C = 37.0-39.0%
- water content = 60.7%

# Type III

- Polyorganosiloxane of general formula (1), wherein R<sub>1</sub> is -OH,
- $R_3$  is -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(H)(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), X + Y = 300-1500,
- % nitrogen (with respect to silicone) = 0.03
- 3.6% of an emulsifier
- 14% of an emulsifiable oxidised polyethylene which has a density of 0.95 to 1.05 g/cm<sup>3</sup> at 20°C, a drop point of 100-150°C, an acid number of 10 to 60 and a saponification number of 15 to 80
- solid content of the emulsion measured by evaporation at 120°C = 23.0-25.0%
- water content = 73.7%

- 30 -

## Type IV

- Polyorganosiloxane of general formula (1), wherein R<sub>1</sub> is -OH,
- $R_3$  is  $-CH_2CH_2CH_2N(H)(CH_2CH_2NH_2)$ , X + Y = 300-1500,
- % nitrogen (with respect to silicone) = 0.11
- 4.3% of an emulsifier
- 0.3% of a fatty acid monoalkanolamide of formula (15b), wherein  $\rm R_{34}$  is hydrogen and  $\rm R_{37}$  is hydrogen or a radical of formula -C(O)R<sub>36</sub>
- solid content of the emulsion measured by evaporation at 120°C = 37.0-39.0%
- water content = 60.7%

### Type V

- Polyorganosiloxane of general formula (1), wherein R1 is -OH,
- $R_3$  is  $-CH_2CH_2CH_2N(H)(CH_2CH_2NH_2)$ , X + Y = 300-1500,
- % nitrogen (with respect to silicone) = 0.11
- 4.4% of an emulsifier
- 0.2% of an emulsifiable oxidised polyethylene which has a density of 0.95 to 1.05 g/cm³ at 20°C, a drop point of 100-150°C, an acid number of 10 to 60 and a saponification number of 15 to 80
- solid content of the emulsion measured by evaporation at 120°C = 37.0-39.0%
- water content = 60.7%

# Type VI

- Polyorganosiloxane of general formula (1), wherein  $R_1$  is -CH<sub>3</sub>,
- $H_3$  is  $-CH_2CH_2CH_2N(H)(CH_2CH_2NH_2)$ , X + Y = 150-300,
- % nitrogen (with respect to silicone) = 0.12
- 11% of an emulsifier
- 0.3% of a fatty acid dialkanolamide of formula (15a), wherein  $R_{34}$ ,  $R_{38}$ ,  $R_{38}$ ' and  $R_{38}$ " are hydrogen or -CH<sub>2</sub>OH
- solid content of the emulsion measured by evaporation at 120°C = 24.0-26.0%
- water content = 72.1%

# Type VII

- Polyorganosiloxane of general formula (1), wherein R<sub>1</sub> is -CH<sub>3</sub>,

 $R_3$  is  $-CH_2CH_2CH_2N(H)(CH_2CH_2NH_2)$ , X + Y = 40-150,

- 31 -

% nitrogen (with respect to silicone) = 0.08

- 13.2% of an emulsifier
- 0.23% of an emulsifiable oxidised polyethylene which has a density of 0.95 to 1.05 g/cm³ at 20°C, a drop point of 100-150°C, an acid number of 10 to 60 and a saponification number of 15 to 80
- solid content of the emulsion measured by evaporation at 120°C = 41.0-43.0%
- water content = 44.4%

### Type VIII

- Polyorganosiloxane of general formula (1), wherein  $R_1$  is -CH<sub>3</sub>,  $R_3$  is -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(H)(CH<sub>2</sub>CH<sub>2</sub>N(H)((CO)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH))), X + Y = 300-1500, % nitrogen (with respect to silicone) = 0.1
- 9.8% of an emulsifier
- 0.1% of an emulsifiable oxidised polyethylene which has a density of 0.95 to 1.05 g/cm³ at 20°C, a drop point of 100-150°C, an acid number of 10 to 60 and a saponification number of 15 to 80
- solid content of the emulsion measured by evaporation at 120°C = 20.5-22.5%
- water content = 76.9%

# Type IX

- Polyorganosiloxane of general formula (8), wherein  $R_{17}$  is -CH<sub>3</sub>,  $R_3$  is CH<sub>3</sub>,  $R_{19}$  is a polyethylenoxide radical,  $X^1+Y^1+S=40$ -150,
- % nitrogen (with respect to silicone) = 0
- 2% of an emulsifier
- 0.15% of an emulsifiable oxidised polyethylene which has a density of 0.95 to 1.05 g/cm³ at 20°C, a drop point of 100-150°C, an acid number of 10 to 60 and a saponification number of 15 to 80
- solid content of the emulsion measured by evaporation at 120°C = 23.0-25.0%
- water content = 74.9%

## Type\_X

- Polyorganosiloxane of general formula (8), wherein R $_{17}$  is -CH $_3$ , R $_3$  is -CH $_2$ CH $_2$ CH $_2$ CH $_2$ NH $_2$ , R $_{19}$  is a polyethylene/polypropyleneoxide radical, X $^1$  + Y $^1$  + S = 150-300

- 32 -

% nitrogen (with respect to silicone) = 0.07

- 3.5% of an emulsifier
- 1.5% of a fatty acid dialkanolamide of formula (15a), wherein  $R_{34}$ ,  $R_{38}$ ,  $R_{38}$  and  $R_{38}$ " are hydrogen or -CH<sub>2</sub>OH
- solid content of the emulsion measured by evaporation at 120°C = 19.5-21.5%
- water content = 73%

### Type XI

- Polyorganosiloxane of general formula (9), wherein  $R_{26}$  is  $C_{12}$ alkyl,  $R_{27}$  is 2-phenylpropyl,  $R_{28}$  is an epoxy radical of formula (10),  $X^2 + X^3 + X^4 + Y^2 = 40$ -150,
- % nitrogen (with respect to silicone) = 0
- 2.9% of an emulsifier
- 0.85% of an emulsifiable oxidised polyethylene which has a density of 0.95 to 1.05 g/cm³ at 20°C, a drop point of 100-150°C, an acid number of 10 to 60 and a saponification number of 15 to 80
- solid content of the emulsion measured by evaporation at 120°C = 37.0-39.0%
- water content = 62%

### Type XII

- Polyorganosiloxane of general formula (1), wherein R<sub>1</sub> is CH<sub>3</sub>, R<sub>3</sub> is C<sub>18</sub>alkoxy,
- X + Y = 40-150, % nitrogen (with respect to silicone) = 0
- 3.2% of an emulsifier
- 1.5% of an emulsifiable oxidised polyethylene which has a density of 0.95 to 1.05 g/cm³ at 20°C, a drop point of 100-150°C, an acid number of 10 to 60 and a saponification number of 15 to 80
- solid content of the emulsion measured by evaporation at 120°C = 34.0-35.5%
- water content = 61.4%

## Type XIII

- Polyorganosiloxane of general formula (1), wherein R<sub>1</sub> is -OH,
- $R_3$  is  $-CH_2CH_2CH_2N(H)(CH_2CH_2NH_2)$ , X + Y = 300-1500.
- % nitrogen (with respect to silicone) = 0.1
- 4.2% of an emulsifier

- 33 -

- 6.2% of a fatty acid monoalkanolamide of formula (15b), wherein  $R_{34}$  is hydrogen and  $R_{37}$  is hydrogen or a radical of formula -C(O) $R_{36}$
- solid content of the emulsion measured by evaporation at 120°C = 38-40%
- water content = 60%

# Type XIV

- Polyorganosiloxane of general formula (8), wherein R<sub>3</sub> is -CH<sub>3</sub> and R<sub>17</sub> is -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>,
   R<sub>19</sub> is a polyethyleneoxide radical, X¹ + Y¹ + S = 40-150,
- % nitrogen (with respect to silicone) = 0.04
- 7.2% of an emulsifier
- solid content of the emulsion measured by evaporation at 120°C = 54-56%
- water content = 38.1%

### Type XV

1 part of emulsion Type XIII and 9 parts of emulsion type XIV

# Example 2 Hydrophilicity

The formulated rinse conditioners (see Table 1) are applied according to the following procedure:

Woven cotton swatches of size of 50 cm by 40 cm are washed together with ballast material (cotton and cotton/polyester) in a AEG Oeko Lavamat 73729 washing machine maintaining the washing temperature at 40°C. The total fabric load of 1 kg is washed for 15 minutes with 33 g of ECE Color Fastness Test Detergent 77 (Formulation January 1977, according to ISO 105-CO6). The rinse conditioner formulation as described in Table 1 is applied in the last rinse cycle at 20°C. After rinsing with the formulation the textile swatches are dried on a washing line at ambient temperature.

# Evaluation of Hydrophilicity

The water absorption of fabrics treated with the test samples is measured by the wicking test. Test strips are fixed to a frame and dipped about 1mm deep in a colored aqueous solution. The rise of water in the strips is measured after twenty minutes. Water absorption

- 34 -

of fabrics treated with rinse conditioner formulations from Table 1 are compared. The average values of four parallel measurements are given in Table 2.

Table 2

Rinse conditioner sample	Measured water rise	
	(cm)	
0 (Reference)	8.2	
A	9.6	
В	10.2	
С	9.5	
D	9.6	
E	9.2	
F	9.0	
G	9.8	
Н	9.1	
	9.2	
J	9.6	
К	9.8	
L	9.6	
М	9.3	

These results show an improved hydrophilicity of the textile fabric material treated with compositions of the present invention.

In all experiments the following textiles have been used:

Cotton woven: 120 g/m2, bleached, with resin finishing: Cotton/Polyester 66/34 woven: 85 g/m2, bleached.

Both textiles were finished with a resin according to Oekotex Standard 100: 30 g/l of modified dimethyloldihydroxyethylene urea ( 70% active material) 9 g/l Magnesiumchloride (with 6 H<sub>2</sub>O) padding with a pick-up of approximately 80%

WO 01/25383

PCT/EP00/09396

- 35 -

Drying at about 110 - 120 °C in a oven followed by a 4 minute curing step at 145 °C.

- 36 -

### WHAT IS CLAIMED IS:

- 1. A method of use of a softener composition for imparting hydrophilicity to textile fibre materials in domestic applications, which softener composition comprises:
- A) a fabric softener;
- B) at least one additive selected from the group consisting of
  - a) a polyethylene, or a mixture thereof,
  - b) a fatty acid alkanolamide, or a mixture thereof,
  - c) a polysilicic acid, or a mixture thereof, and
  - d) a polyurethane, or a mixture thereof; and
- C) a dispersed polyorganosiloxane of formula (1)

$$(1) \quad \vec{R'} - \underbrace{\begin{matrix} CH_3 \\ \vdots \\ CH_3 \end{matrix}}_{CH_3} - \underbrace{\begin{matrix} CH_3 \\ \vdots$$

wherein

R1 is OH, OR2 or CH3

R2 is CH3 or CH2CH3

R3 is C1-C20alkoxy, CH3, CH2CHR4CH2NHR5, or CH2CHR4CH2N(COCH3)R5

(2) 
$$(CH_2)_3O$$
 NR<sup>8</sup>

Or (3)  $(CH_2)_3NH$  CH

Or (4)  $(CH_2)_3$  NR<sup>8</sup>

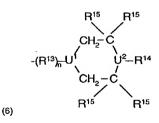
R4 is H or CH2

- 37 -

 $R^5$  is H,  $CH_2CH_2NHR^6$ ,  $C(=O)-R^7$  or  $(CH_2)_2-CH_3$  z is 0 to 7  $R^6$  is H or  $C(=O)-R^7$   $R^7$  is  $CH_3$ ,  $CH_2CH_3$  or  $CH_2CH_2CH_2OH$   $R^8$  is H or  $CH_3$  the sum of X and Y is 40 to 4000;

or a dispersed polyorganosiloxane which comprises at least one unit of the formula (5)

wherein 
$$\begin{split} R^9 &\text{ is } CH_3, CH_3CH_2 \text{ or Phenyl} \\ R^{10} &\text{ is } \text{-O-Si or -O-R}^9 \\ &\text{ the sum of } v \text{ and } w \text{ equals } 3, \text{ and } v \text{ does not equal } 3 \\ A &= \text{-CH}_2CH(R^{11})(CH_2)_K \\ B &= \text{-NR}^{12}((CH_2)_1\text{-NH})_mR^{12}, \text{ or } \end{split}$$



n is 0 or 1 when n is 0,  $U^1$  is N, when n is 1,  $U^1$  is CH i is 2 to 8 k is 0 to 6 m is 0 to 3  $R^{11}$  is H or CH<sub>3</sub>  $R^{12}$  is H,  $C(=O)-R^{16}$ ,  $CH_2(CH_2)_pCH_3$  or

- 38 -

p is 0 to 6

R13 is NH, O, OCH2CH(OH)CH2N(Butyl), OOCN(Butyl)

R<sup>14</sup> is H, linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl, Phenyl or CH<sub>2</sub>CH(OH)CH<sub>3</sub>

R15 is H or linear or branched C1-C4 alkyl

R16 is CH3, CH2CH3 or (CH2)0OH

a is 1 to 6

U2 is N or CH;

# or a dispersed polyorganosiloxane of the formula (8)

$$(8) \quad R^{17} = \begin{array}{c|c} CH_3 & CH_3 &$$

## wherein

R3 is as previously defined

R17 is OH, OR18 or CH2

R18 is CH3 or CH2CH3

R<sup>19</sup> is R<sup>20</sup>-(EO)<sub>m</sub>-(PO)<sub>a</sub>-R<sup>21</sup>

m is 3 to 25

n is 0 to 10

R<sup>20</sup> is the direct bond or CH<sub>2</sub>CH(R<sup>22</sup>)(CH<sub>2</sub>)<sub>o</sub>R<sup>23</sup>

p is 1 to 4

R21 is H, R24, CH2CH(R22)NH2 or CH(R22)CH2NH2

R22 is H or CH3

R23 is O or NH

R24 is linear or branched C1-C8 alkyl or Si(R25)3

R<sup>25</sup> is R<sup>24</sup>, OCH<sub>3</sub> or OCH<sub>2</sub>CH<sub>3</sub>

EO is -CH2CH2O-

- 39 -

PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)Othe sum of X<sub>1</sub>,Y<sub>1</sub> and S is 20 to 1500;

or a dispersed polyorganosiloxane of the formula (9)

wherein

R26 is linear or branched C1 - C20 alkoxy, CH2CH(R4)R29

R4 is as previously defined

R29 is linear or branched C1 - C20 alkyt

 $R^{27}$  is aryl, aryl substituted by linear or branched  $C_1$  -  $C_{10}$  alkyl, linear or branched  $C_1$  -  $C_{20}$  alkyl substituted by aryl or aryl substituted by linear or branched  $C_1$  -  $C_{10}$  alkyl  $R^{20}$  is

the sum of  $X^2$ ,  $X^3$ ,  $X^4$  and  $Y^2$  is 20 to 1500, wherein  $X^3$ ,  $X^4$  and  $Y^2$  may be independently of each other 0;

or a mixture thereof.

2. A method of use according to claim 1 wherein the polyorganosiloxane is of formula (1):

$$(1) \quad \overrightarrow{R} = \underbrace{\begin{array}{c} CH_3 \\ \vdots \\ Si = 0 \\ \vdots \\ CH_3 \end{array}}_{CH_3} \underbrace{\begin{array}{c} CH_3 \\ \vdots \\ CH_3 \end{array}}_{X} \underbrace{\begin{array}{c} CH_3 \\ \vdots \\ R^3 \end{array}}_{CH_3} \underbrace{\begin{array}{c} CH_3 \\ \vdots \\ CH_3 \end{array}}_{CH_3}$$

wherein

R¹ is OH, OR² or CH₃

R2 is CH3 or CH2CH3

R3 is C1-C20alkoxy, CH3, CH2CHR4CH2NHR5, or

- 40 -

 $R^4$  is H or CH<sub>3</sub>  $R^5$  is H, CH<sub>2</sub>CH<sub>2</sub>NHR<sup>6</sup>, C(=O)-R<sup>7</sup>  $R^6$  is H or C(=O)-R<sup>7</sup>  $R^7$  is CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub> or CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH  $R^8$  is H or CH<sub>3</sub> the sum of X and Y is 40 to 4000;

or a dispersed polyorganosiloxane which comprises at least one unit of the formula (5);

wherein

 $R^9$  is  $CH_3$ ,  $CH_3CH_2$   $R^{10}$  is -O-Si or -O- $R^9$ the sum of v and w equals 3, and v does not equal 3  $A = -CH_2CH(R^{11})(CH_2)_K$ B =

$$R^{15}$$
  $R^{15}$   $CH_2$   $CH_2$   $CH_2$   $CH_2$   $CH_2$   $CH_3$   $CH_2$   $CH_3$   $CH_4$   $CH_5$   $CH_$ 

- 41 -

n is 1
U<sup>1</sup> is CH
k is 0 to 6
R<sup>11</sup> is H or CH<sub>3</sub>
R<sup>13</sup> is OOCN(Butyl)
R<sup>14</sup> is H, linear C<sub>1</sub>-C<sub>4</sub> alkyl, Phenyl
R<sup>15</sup> is H or linear C<sub>1</sub>-C<sub>4</sub> alkyl
U<sup>2</sup> is N:

or a dispersed polyorganosiloxane of the formula (8):

$$(8) \quad R^{17} = \begin{array}{c} CH_3 & C$$

wherein

R3 is as previously defined

R<sup>17</sup> is OH, OR<sup>18</sup> or CH<sub>3</sub>

R18 is CH3 or CH2CH3

 $R^{19}$  is  $R^{20}$ -(EO)<sub>m</sub>-(PO)<sub>0</sub>- $R^{21}$ 

m is 3 to 25

n is 0 to 10

R<sup>20</sup> is the direct bond or CH<sub>2</sub>CH(R<sup>22</sup>)(CH<sub>2</sub>)<sub>0</sub>R<sup>23</sup>

p is 1 to 4

 $R^{21}$  is H,  $R^{24}$ ,  $CH_2CH(R^{22})NH_2$  or  $CH(R^{22})CH_2NH_2$ 

R<sup>22</sup> is H or CH<sub>3</sub>

R<sup>23</sup> is O or NH

R24 is linear or branched C1-C3 alkyl or Si(R25)3

R25 is R24, OCH3 or OCH5CH3

EO is -CH<sub>2</sub>CH<sub>2</sub>O-

PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)O-

- 42 -

the sum of X<sub>1</sub>,Y<sub>1</sub> and s is 20 to 1500:

or a dispersed polyorganosiloxane of the formula (9);

$$(9) \quad H_{3}C = \begin{matrix} CH_{3} \\ I \\ SI \\ CH_{3} \end{matrix} = \begin{matrix} CH_{3} \\ I \\ SI \\ CH_{3} \end{matrix} = \begin{matrix} CH_{3} \\ I \\ SI \\ CH_{3} \end{matrix} = \begin{matrix} CH_{3} \\ I \\ SI \\ CH_{3} \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \\ I \end{matrix} = \begin{matrix} CH_{3} \\ I \end{matrix} = \begin{matrix} CH_$$

wherein

R<sup>26</sup> is linear C<sub>1</sub> - C<sub>20</sub> alkoxy,

R4 is as previously defined

R29 is linear C1 - C20 alkyl

R27 is, CH2CH(R4)Phenyl

R<sup>28</sup> is

the sum of  $X^2$ ,  $X^3$ ,  $X^4$  and  $Y^2$  is 20 to 1500, wherein  $X^3$ ,  $X^4$  and  $Y^2$  may be independently of each other 0;

or a mixture thereof.

 A method of use according to claim 1 or 2 wherein a polyorganosiloxane of formula (1) is used, wherein

R1 is OH or CH3,

R3 is CH3, C10-C20alkoxy or CH2CHR4CH2NHR5.

R⁴ is H.

R5 is H or CH2CH2NHR6,

R6 is H or C(=0)-R7, and

R7 is CH3, CH2CH3 or especially CH2CH2CH2OH.

 A method of use according to claim 1 or 2 wherein a polyorganosiloxane of formula (8) is used, wherein

R3 is CH3, C10-C20alkoxy or CH2CHR4CH2NHR5,

- 43 -

 $R^4$  is H,  $R^5$  is H or  $CH_2CH_2NHR^6$ ,  $R^6$  is H or  $C(=O)-R^7$ ,  $R^7$  is  $CH_2CH_3$ ,  $CH_2CH_2CH_2OH$  or especially  $CH_3$ , and  $R_{17}$  is  $CH_3$  or OH.

- 5. A method of use according to claim 1 or 2 wherein a polyorganosiloxane of formula (9) is used, wherein  $R^{26}$  is  $CH_2CH(R^4)R^{29}$ ,  $R^4$  is H, and
- R<sup>27</sup> is 2-phenyl propyl.
- A method of use according to any of claims 1 to 5 wherein the composition is a liquid aqueous composition.
- 7. A method of use according to any of claims 1 to 5 wherein the composition is used in a tumble dryer sheet composition.
- 8. A method of use according to any of claims 1 to 7 in which the polyorganosiloxane is nonionic or cationic.
- A method of use according to any of claims 1 to 8 in which the composition has a solids content of 5 to 70 % at a temperature of 120°C.
- 10. A method of use according to any of claims 1 to 9 in which the composition contains a water content of 25 to 90 % by weight based on the total weight of the composition.
- 11. A method of use according to any of claims 1 to 10 in which the composition has a pH value from 2 to 7.
- 12. A method of use according to any of claims 1 to 11 in which the nitrogen content of the aqueous emulsion due to the polyorganosiloxane is from 0 to 0.25 % with respect to the silicon content.

- 44 -

- 13. A method of use according to any of claims 1 to 12 wherein the composition comprises a polyethylene, a fatty acid alkanolamide or a polyurethane.
- 14. A method of use according to any of claims 1 to 13 wherein the composition comprises a polyethylene or a fatty acid alkanolamide.
- 15. A method of use according to any of claims 1 to 14 wherein the composition comprises a fatty acid alkanolamide.
- 16. A method of use according to any of claims 1 to 14 wherein the composition comprises a polyethylene.
- 17. A method of use according to any of claims 1 to 16 wherein the composition is prepared by mixing a preformulated fabric softener with an emulsion comprising the polyorganosiloxane and the additive.
- 18. A method of use according to any of claims 1 to 17 wherein composition has a clear appearance.
- 19. A method of use according to any of claims 1 to 18 in which the composition comprises:
- a) 0.01 to 70 % by weight, based on the total weight of the composition, of a polyorganosiloxane, or a mixture thereof;
- b) 0.2 to 15 % by weight based on the total weight of an emulsifier, or a mixture thereof;
- c) 0.01 to 15 % by weight based on the total weight of at least one additive selected from the group consisting of a polyethylene, a fatty acid alkanolamide, a polysilicic acid and a polyurethane, and
- d) water to 100 %.
- 20. A tumble dryer sheet comprising a composition as defined in claim 1.

### (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

## (19) World Intellectual Property Organization International Bureau



# 

(43) International Publication Date 12 April 2001 (12.04.2001)

PCT

(10) International Publication Number WO 01/25383 A1

- (51) International Patent Classification7:
- C11D 3/37.
- 86462 Langweid (DE), GORETZKI, Ralf [DE/DE]; Berliner Allce 22B, 86153 Augsburg (DE). WEBER, Barbara [DE/DE]; Schlossweg 1, 79639 Grenzach-Wyhlen (DE). MARTIN, Emmanuel [FR/FR]; 4, Cité Beaulien, F-68300 Saint Louis Neuweg (FR).

- 17/04, 3/12, 1/645, 1/62
- (21) International Application Number: PCT/EP00/09396
- (22) International Filing Date:
  - 26 September 2000 (26.09.2000)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 99810899.7

5 October 1999 (05.10.1999) EP

- (71) Applicants (for all designated States except US): CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH). CIBA SPEZIALITÄTENCHEMIE PFERSEE GMBH [DE/DE]; Rehlinger Strasse 1, 86462 Langweid a. Lech
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): KVITA, Petr [CH/CH]; Binningerstrasse 4D, 4153 Reinach (CH). OTTO, Peter [US/DE]; Ritterstrasse 26, 79618 Rheinfelden (DE). DUBINI, Mario [CH/CH]; Härgelenstrasse 29, CH-4435 Niederdorf (CH). CHROBACZEK, Harald [DE/DE]; Oblatterwallstrasse 38, 86153 Augsburg (DE). GEUBTNER, Michael [DE/DE]; Aggensteinstrasse 5,

- (74) Common Representative: CIBA SPECIALTY CHEMI-CALS HOLDING INC.; Patentabteilung, Klybeckstrasse 141, CH-4057 Basel (CH).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU. AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, IP, KE, KG, KP, KR, KZ, LC, LK, LR, LS. LT. LU. LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

### Published:

With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginrung of each regular issue of the PCT Gazette.

(54) Title: FABRIC SOFTENER COMPOSITIONS

(57) Abstract: The present invention relates to a method of use of a softener composition for imparting hydrophylicity to textile fibre materials in domestic applications, which softener composition comprises; A) a fabric softener; B) at least one additive selected from the group consisting of a) a polyethylene, or a mixture thereof, b) a fatty acid alkanolamide, or a mixture thereof, c) a polysilicie acid, and d) a polyurethane; C) selected polyorganosiloxanes.



US Case HF/5 -22102/US/A

# **DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATIONS**

	Original		Supplementa	al 🗆	Substitu	te 🛭	<u>s</u> 1	PCT
As a below named inventor, I hereby declare that:								
My residence, post office address and citizenship are as stated below next to my name.								
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if more than one name is listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled								
FABRIC SOFTENER COMPOSITIONS								
which is described and claimed in:								
	the attached specification.							
	the spe filed _	cification (day/month		ation No. as amended o		(day/month/year)	_ (if	applicable).
×	filed _	cification 26/09/i (day/month/		al Application	No. F	PCT/EP 00/09396	i	
	assigne	ed U.S. Ap	plication No.		(	if applicable), ai	nd a	ıs amended
	□ und	der PCT A	rticle 19 on	(day/month	/vear) (i	if applicable)		
	□ und	der PCT A	rticle 34 on	(day/month	(1	if applicable)		
	□ and	d further a	mended on	(day/month	(i	if applicable)		
I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.								
I acknowledge the duty to disclose all information which is known by me to be material to the patentability of this application as defined in 37 C.F.R. § 1.56.								

I hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America relating to this subject matter having a filing date before that of the

csc

application on which priority is claimed:

indrara, comma

COUNTRY/REGION (OR PCT)	APPLICATION No	•	FILING (day/mon			PRIORITY CLAIMED		MED	
Europe (designating DE)	99810899,7		05/10	)/99	0	₫ \	res .		No
						י ב	⁄es		No
					E	J `	res -		No
						] '	⁄es		No
					C	` د	⁄es		No
I hereby claim the benefit under 35 U.S.C. § 119 (e) of any United States provisional application(s) listed below:									
APPLICATION NO.			FILING DA (day/month/y						
I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or PCT international application(s) designating the United States listed below and, insofar as the application discloses and claims subject matter in addition to that disclosed in the prior copending application, I acknowledge the duty to disclose all information known by me to be material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:									
U.S. APPLICATION No.	FILING DATE (day/month/year)				STATU	ıs			
			Patented		Pendin	g		Aban	doned
			Patented		Pendir	g		Aban	doned
			Patented		Pendin	g		Aban	doned
			Patented		Pendir	g		Aban	doned
			Patented		Pendir	ıg		Aban	doned
PCT APPLICATION No. (designating the U.S.)	. FILING DATE		U.S. APPLICATION No. (if any)		ΓΙΟΝ	STATUS			
							Pate	nted	
•							Pend	ding	
							Aba	ndone	d

US 01/00 /2

I hereby appoint the following attorneys and agents, associated with Customer No. 000324, each of them with full power of substitution, revocation and appointment of associates, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Luther A. R. Hall (Reg. No. 27,337), JoAnn L. Villamizar (Reg. No. 30,598), Kevin T. Mansfield (Reg. No. 31,635), David R. Crichton (Reg. No. 37,300), Michele A. Kovaleski (Reg. No. 37,865) and Tyler A. Stevenson (Reg. No. 46,388).

Address all correspondence associated with Customer No. 000324 o Ciba Specialty Chemicals Corporation, Patent Department, 540 White Plains Road, P.O. Box 2005, Tarrytown, NY 10591-9005.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first joint inventor

Petr KVITA

Inventor's signature

\_\_\_\_ Date

Binningerstrasse 4D

4153 Reinach Switzerland

Citizenship

Residence

Swiss

Post Office Address

same as above

CSC

US 01/00 /4

	Full name of second joint inventor, if any	Peter OTTO		
	Inventor's signature	P.Oth	Date _	12.3.02 (day/month/year)
700	Residence	Ritterstrasse 26 79618 Rheinfelden Gernfany		
<i>A</i>	Citizenship	American		
	Post Office Address	same as above		
3	Full name of third joint inventor, if any	Mario DUBINI		
~6	Inventor's signature	_ UU	Date /	(day/month/year)
3"	Residence	Härgelenstrasse 29 4435 Niederdorf Switzerland		
	Citizenship	Swiss		
	Post Office Address	same as above		
-	Full name of fourth joint inventor, if any	Harald CHROBACZEK		
0	Inventor's signature	A. Milwa	Date _	05.03.02 (day/month/year)
40	Residence	Oblatterwallstrasse 38 86153 Augsburg DEX Germany		
•	Citizenship	German		
	Post Office Address	same as above		

	Full name of fifth joint inventor, if any	Michael GEUBTNER	·	
	Inventor's signature	G. flustre	_ Date	06.01.02 (day/month/year)
) F	) Residence	Aggensteinstrasse 5 86462 Langweid DEX Germany		
	Citizenship	German		
	Post Office Address	same as above		
	Full name of sixth joint inventor, if any	Ralf GORETZKI		
/ P	Inventor's signature	Jonan	Date	OJ.OJ.OZ (day/month/year)
I	Residence	Kornstrasse 9a 86391 Stadtbergen DEX Germany		
	Citizenship	German		
	Post Office Address	same as above		
•	Full name of seventh joint inventor, if any	Barbara WEBER		
100	Inventor's signature	B. Webot	Date	/3.03.02 (day/month/year)
	Residence	Schlossweg 1 79639 <u>Grenzach-Wyhlen</u> DEX Germany		
	Citizenship	German		
	Post Office Address	same as above		
	csc			US 01/00 /5

200

Full name of eighth joint inventor, if any

Emmanuel MARTIN

Inventor's signature

Dat

13/03/02

500

Residence

4, Cité Beaulieu

68300 Saint Louis Neuweg

France

FLX

Citizenship

French

Post Office Address

same as above